Wisconsin Mercury Deposition Network Summary Report

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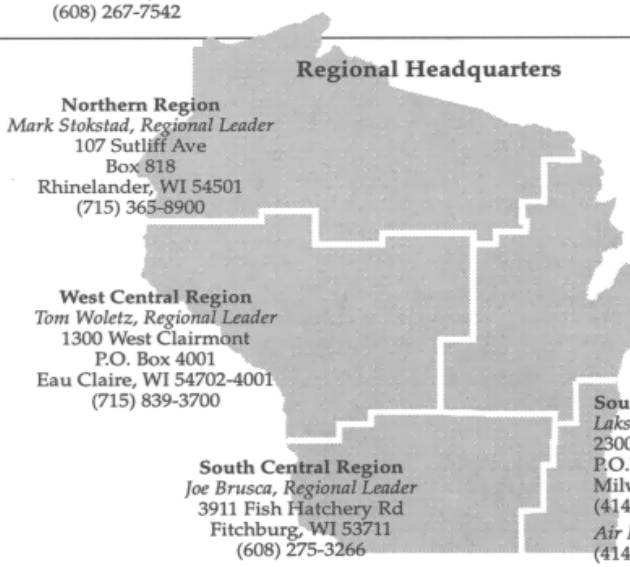

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Introduction:

Atmospheric deposition is thought to be a major pathway for mercury to enter the Wisconsin environment. In the chain of events from the initial volatilization of mercury or suspension of mercury compounds into the atmosphere to its accumulation in fish-eating organisms, the washing of mercury from the atmosphere by various forms of precipitation constitutes a critical step in the availability of this toxin. This step provides a logical point at which to monitor mercury levels and determine loading rates to local environments due to wet deposition. A comprehensive program to quantify mercury concentration in rain and to develop deposition loading is critical to developing a better understanding of the atmospheric deposition pathway.

Since 1994, atmospheric mercury deposition has been monitored at a network of sites in the State of Wisconsin by the Department of Natural Resources (WDNR) with the Wisconsin Mercury Deposition Monitoring Network (WMDN) (Figure 1). The WMDN consists of seven monitoring stations, operated by the WDNR's Air Management Bureau, designed to collect information on the total (wet and dry) mercury deposition to the environment. The network makes use of a passive sampler based on a design used successfully in Sweden by the Swedish Environmental Research Institute (Institutet för Vatten- och Luftvårdsforskning (IVL)).

This report provides summary analysis of the WMDN data for the period January 1998 to April 1, 1999. Statistical data analysis includes annual and seasonal concentration and deposition values. When appropriate, the statistical test is noted and a value is stated. Mean values are reported with the standard error, an indicator of variance in the data related to the sample size.

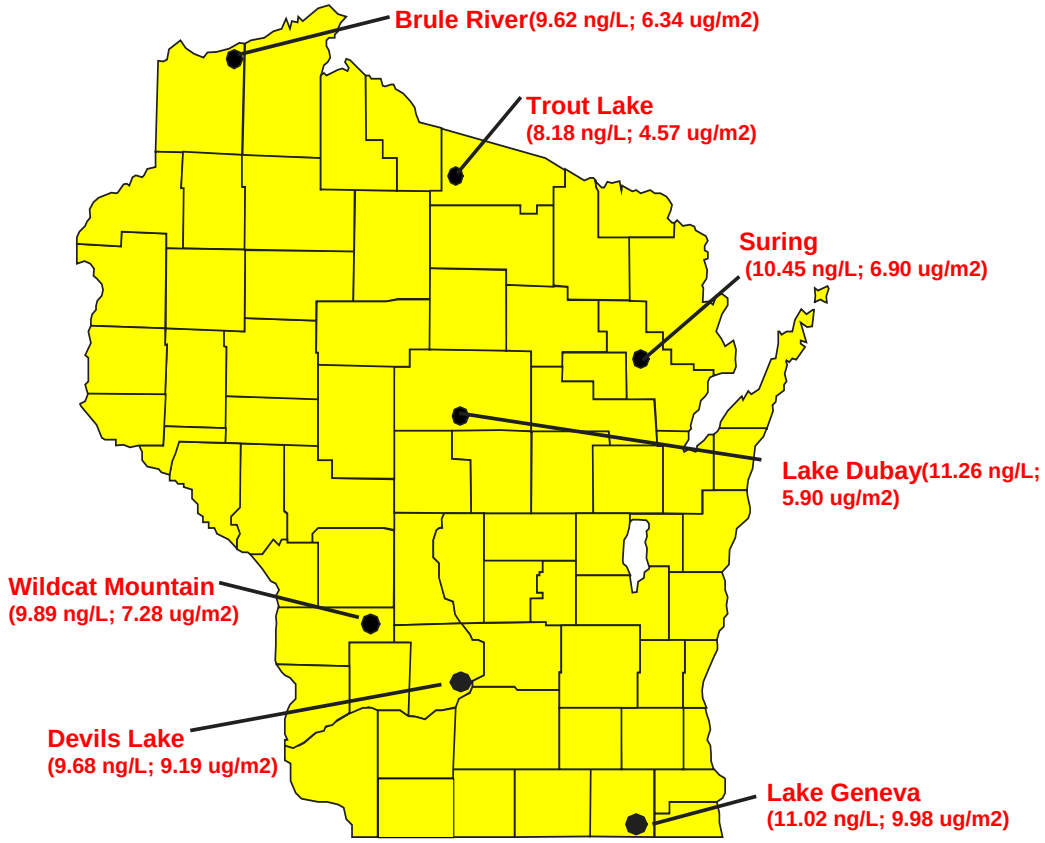
A recent mercury deposition data report summarizes the data results for the period 1995-1997 and includes a detailed narrative of the Wisconsin IVL (WIVL) Mercury Deposition Network. Please see the "Wisconsin Mercury Deposition Network Report 1995-1997" (Publication #: PUB-AM-302-99); this Department of Natural Resources publication is also available at the following web site:

http://www.dnr.state.wi.us/org/aw/air/MONITOR/mercury9597.pdf

Summary of Findings:

- The statewide mean mercury concentration is 9.84 ± 0.37 ng/L for the report period.
- The statewide mean precipitation weighted concentration, (i.e., volume weighted concentration) of 9.68 ng/L, is slightly lower than the statewide mean mercury concentration.
- Annual deposition in 1998 ranged from a minimum of 4.57 $\mu g/m^2$ at the northern remote site, Trout Lake, on the A-sampling train and a maximum of 9.98 $\mu g/m^2$ at the Lake Geneva site in southern Wisconsin.
- The statewide mean annual deposition in 1998 was 6.89 $\mu g/m^2$.
- An empirical increase in deposition exists from north to south in Wisconsin.
- The statewide mean weekly deposition value in 1998 is 0.15 ± 0.01 $\mu g/m^2$.
- A comparison of northern and southern sites indicates that significantly greater amount of mercury was deposited on a weekly basis at southern sites than northern sites in 1998 (north = 0.12 ± 0.01 $\mu g/m^2$ and south 0.19 ± 0.02 $\mu g/m^2$).
- A strong statistical relationship between precipitation and deposition exists among the sites. This suggests that wet deposition is largely responsible for atmospheric mercury deposition measured with the WIVL passive monitor on an annual basis.
- Wet deposition is directly responsible for approximately two-thirds (67%) of atmospheric mercury deposition during any given week.
- Significantly more mercury is deposited in Wisconsin during the spring and summer seasons than in the winter and fall.
- Site locations with precipitation weighted concentrations and total annual mercury deposition are included in the Figure 1.
- There is poor inter-laboratory agreement between the collocated sampling trains at Trout Lake.
- Data completeness in 1998 was good to excellent at all monitoring sites. The mean percentage of complete samples for all sites is 87%.

Figure 1
Wisconsin Mercury Deposition Network Sites



(Values contained in parentheses are the 1998 precipitation weighted concentration and total annual deposition)

Mercury Concentration:

Mean Mercury Concentration:

The 1998 mean mercury concentrations with their standard errors are depicted in Figure (2) and displayed in Table (1). The mean concentrations among all of the sites are not significantly different at the 0.05 level. Based on an ANOVA, the p-value resulting from the site comparison is ($p \leq 0.074$). The statewide mean concentration is 9.84 ± 0.37 ng/L, a widely accepted value in the literature.

Figure 2
1998 Annual Mean Mercury Concentration
with Standard Error Bars

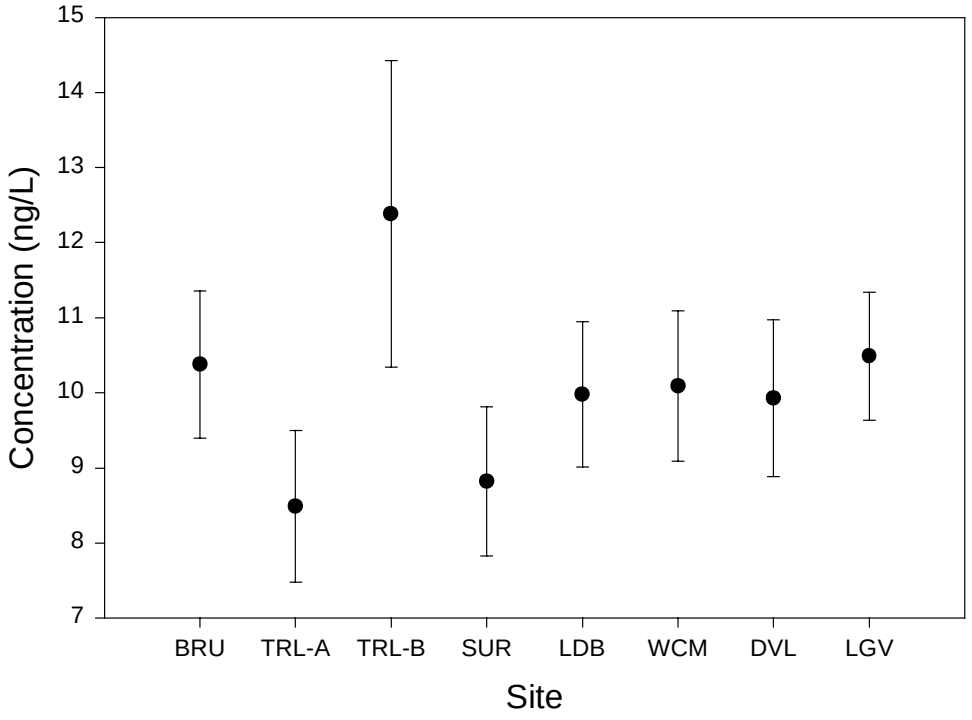


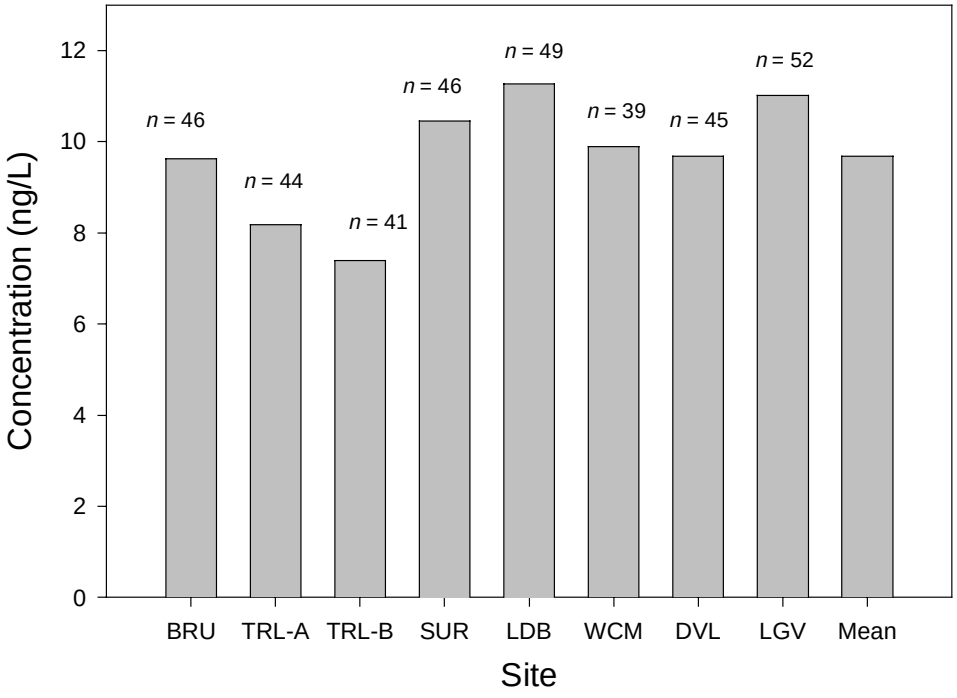
Table 1: Annual Data Summary for IVL Mercury Deposition Network 1998				
Site	**Sample Size (*n*)**	**Mean Concentration (ng/L)**	**Precipitation Weighted Conc. (ng/L)**	**Total Deposition ($\mu g/m^2$)**
BRU	46	10.38±0.98	9.62	6.34
TRL-A	44	8.49±1.01	8.18	4.57
TRL-B	44 [1]	12.38±2.04	7.39	4.93
SUR	46	8.82±0.99	10.45	6.90
LDB	49	9.98±0.97	11.26	5.90
WCM	39 [2]	10.09±1.0	9.89	7.28
DVL	45	9.93±1.04	9.68	9.19
LGV	52	10.49±0.85	11.02	9.98
Statewide Annual Mean	45	9.84 ± 0.37	9.68	6.89

[1] – This value includes two suspicious, but not invalid, data points during the weeks of 2/10/98 and 2/24/98.
[2] – WCM data missing largely in January, February, and September

Annual Precipitation Weighted Concentration:

Annual precipitation weighted concentrations were calculated for each site in 1998. Values ranged from a minimum of 7.39 ng/L on the TRL-B sampler to a maximum of 11.26 ng/L measured with the LDB sampling train (Table 1) and (Figure 3). On average, these values tend to be less than precipitation weighted concentrations found in the 1995-1997 mercury data report, but the differences are not statistically significant, and no conclusions about downward trends may be drawn. The 1998 statewide mean volume weighted concentration is 9.68 ng/L.

Figure 3
1998 Precipitation Weighted Concentrations

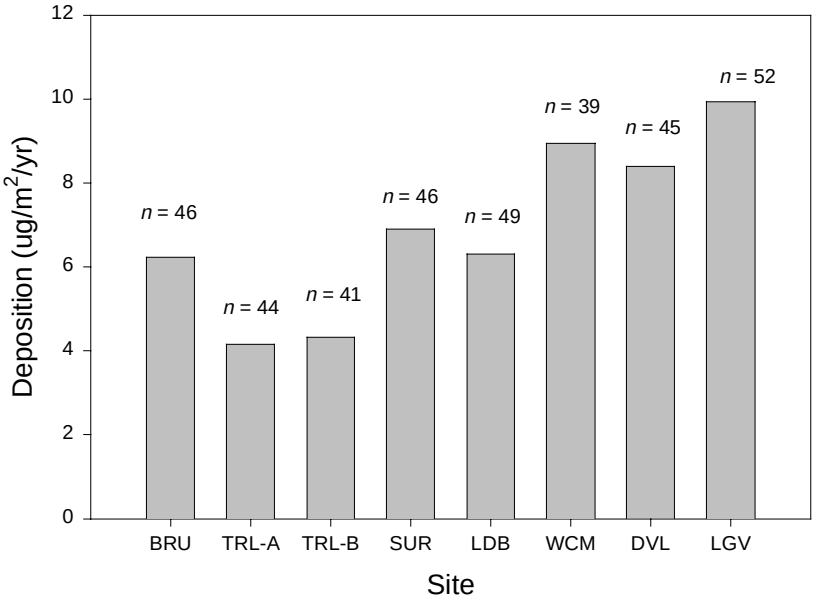


Mercury Deposition:

Annual Total Deposition:

Total deposition values do not exceed 10 μg/m^2 in 1998 (Table 1) & (Figure 4). The minimum total deposition value resulted at Trout Lake, the remote north central site, on the A-sampling train (4.58 μg/m^2). Interestingly, the maximum total deposition value was greater than twice the minimum value and was recorded at Lake Geneva (9.80 μg/m^2) in southeastern Wisconsin. These results support a deposition pattern witnessed in previous years, an empirical increase in deposition from north to south.

Figure 4
1998 Total Annual Mercury Deposition

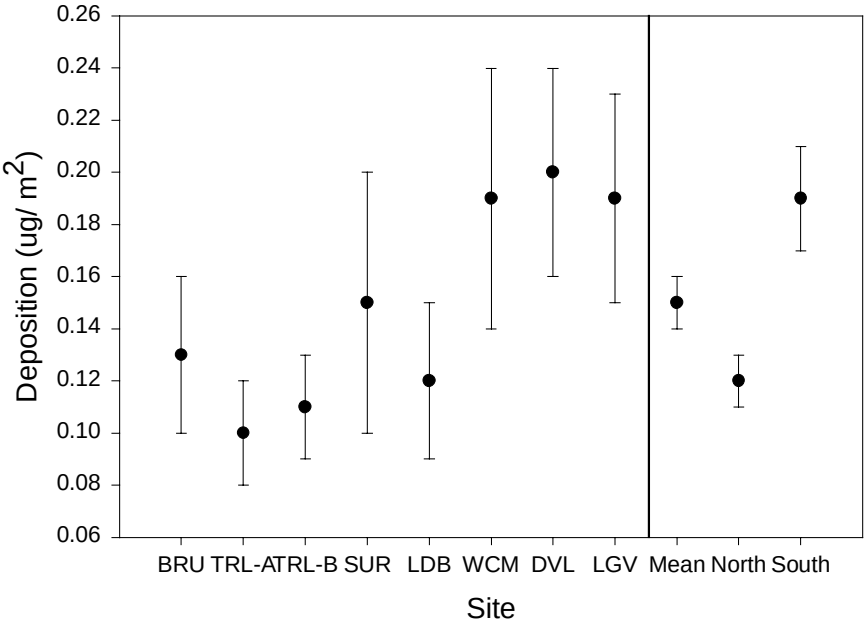


Mean Weekly Deposition:

In 1998, mean weekly deposition values follow a similar pattern to total deposition and are depicted in (Figure 5). Mean weekly deposition values range from a minimum of 0.10 ± 0.02 μg/m^2 at Trout Lake on the A-sampler to a maximum of 0.20 ± 0.04 μg/m^2 at Devils Lake in south central Wisconsin. This range of values is similar to the range of mean weekly deposition values in previous years. The statewide mean weekly deposition value in 1998 is 0.15 ± 0.01 μg/m^2.

Mean weekly deposition values from all sites were compared by means of an ANOVA. There was no statistical difference among the sites in 1998 ($p \leq 0.375$). A comparison of northern sites (BRU, TRL, SUR & LDB) and southern sites (WCM, DVL & LGV), however, indicates that, on a weekly basis, significantly more mercury was deposited at the southern sites than northern sites in 1998 (north = 0.12 ± 0.01 μg/m^2 and south 0.19 ± 0.02 μg/m^2), a difference significant at the ($p \leq 0.01$) level.

Figure 5
1998 Mean Weekly Deposition
with Standard Error

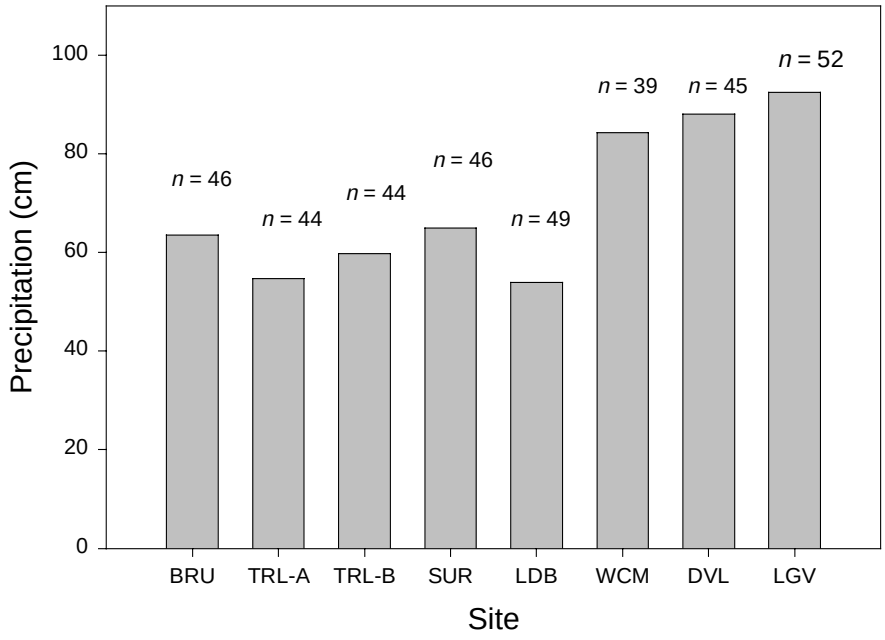


Precipitation:

Total Annual Precipitation:

Precipitation is measured at every site with a Beaufort rain gauge. In 1998, more precipitation fell at southern sites than central and northern sites (Figure 6). Precipitation total values ranged from 52.37 cm/yr. (20.62 in./yr) at Lake DuBay in central Wisconsin to a maximum of 93.78 cm/yr. (36.92 in./yr) at Devils Lake in south central Wisconsin.

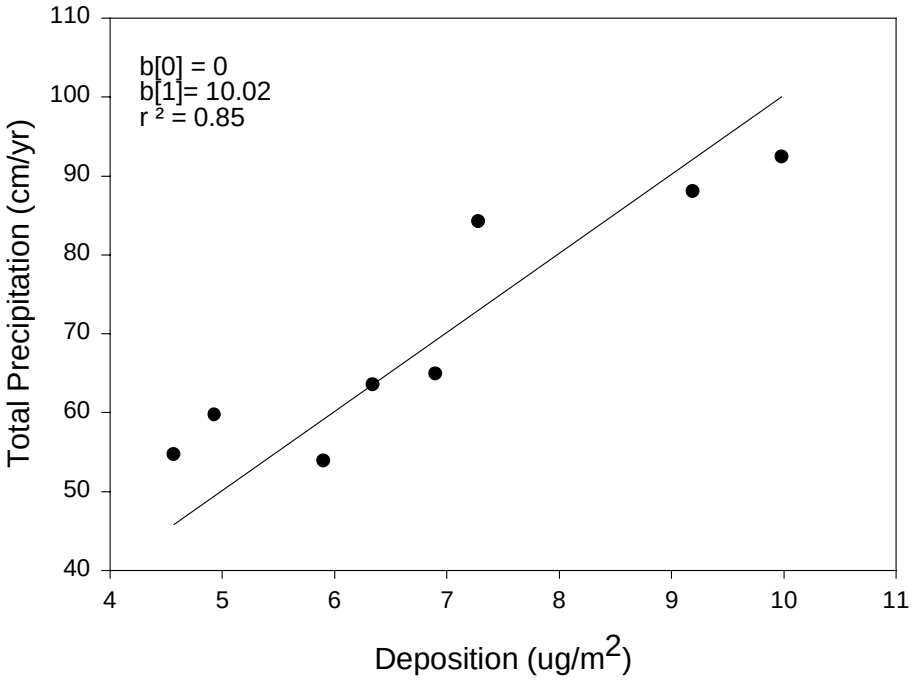
Figure 6
1998 Total Annual Precipitation



Total Precipitation v. Total Deposition Regression Analysis:

A linear regression analysis was performed on the 1998 total annual precipitation and total annual deposition data. The resultant R^2 value of 0.85 indicates a strong statistical relationship between precipitation and deposition among the sites (Figure 7). This suggests that wet deposition is largely responsible for atmospheric mercury deposition measured with the IVL passive monitor on an annual basis.

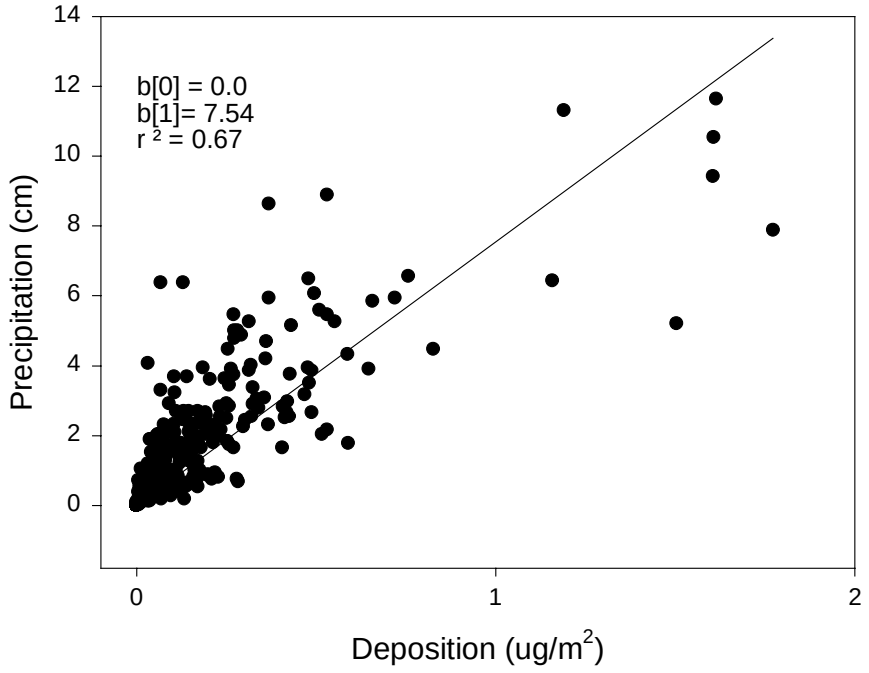
Figure 7
Regression Total Annual Precipitation
vs Total Annual Deposition



Weekly Precipitation v. Weekly Deposition:

As depicted in Figure 8, linear regression analysis was performed on the 1998 *weekly* precipitation and *weekly* deposition data. The resultant R^2 value of 0.67 indicates a moderately strong statistical relationship between *weekly* precipitation and deposition at all of the sites. This more detailed inspection of the relationship between precipitation and deposition may suggest that, on average, wet deposition is directly responsible for approximately two-thirds (67%) of atmospheric mercury deposition during any given week. The remaining 33% of atmospheric deposition may be due to dry deposition or other reasons beyond the scope of this report.

Figure 8
Regression of 1998 Weekly Precipitation against Weekly Deposition



Seasonal Data Analysis:

Seasonal Precipitation:

Seasonal precipitation totals were calculated for each site based on Beaufort raingauge results. As mentioned in the previous subsection, there is a strong relationship between precipitation and deposition. A visual comparison of the seasonal deposition (Fig. 12) and seasonal precipitation (Fig. 9) figures shows strong similarities in the patterns. Table 2 provides a seasonal comparison of all sites for 1998 and the winter of 1999.

Figure 9
1998/99 Seasonal Precipitation

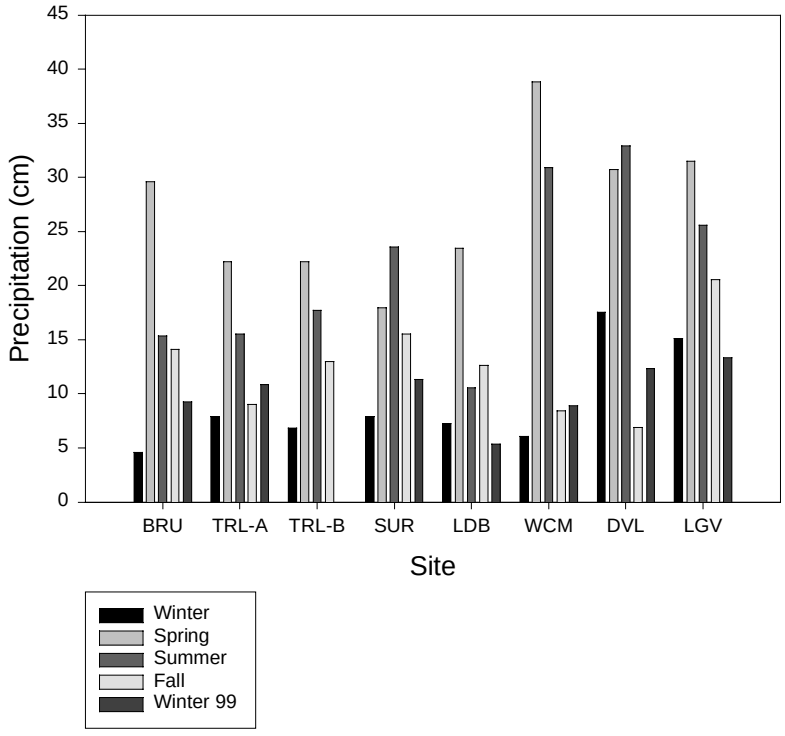


Table 2: 1998/1999 Seasonal Precipitation Totals (cm)						
Site	**Winter**	**Spring**	**Summer**	**Fall**	**Winter 1999**	**1998 TOTAL [1]**
BRU	4.57	29.59	15.32	14.1	9.27	63.58
TRL-A	7.92	22.23	15.52	8.99	10.85	54.66
TRL-B	6.81	22.23	17.68	13	*	59.72
SUR	7.92	17.96	23.55	15.52	11.28	64.95
LDB	7.24	23.47	10.57	12.62	5.33	53.9
WCM	6.05	38.84	30.91	8.43	8.89	84.23
DVL	17.53	30.73	32.89	6.91	12.32	88.06
LGV	15.09	31.52	25.27	20.57	13.36	92.45

[1] Total excludes the winter 1999 deposition data.
* Data not available for TRL-B in 1999.

Seasonal Concentrations:

WIVL mercury samples were collected once a week on Tuesday throughout the year. For this reason, a season begins on the first Tuesday on or after the equinox or solstice and includes the following 13 weeks. Seasonal mercury concentrations were calculated for each site. For representation purposes, separate mean concentration graphs for northern and southern sites were created. The maximum mean seasonal mercury concentration varies from site to site (Figures 10 & 11) (Table 3), however, at most sites in 1998, it occurs in the spring. The summer generally has the second highest mean seasonal mercury concentration. At some sites, winter either has the highest or second highest mean maximum seasonal concentration. The minimum mean seasonal concentration often occurs in either the fall or winter, although there are exceptions.

Figure 10
1998/99 Seasonal Mean Concentrations
at Northern Sites

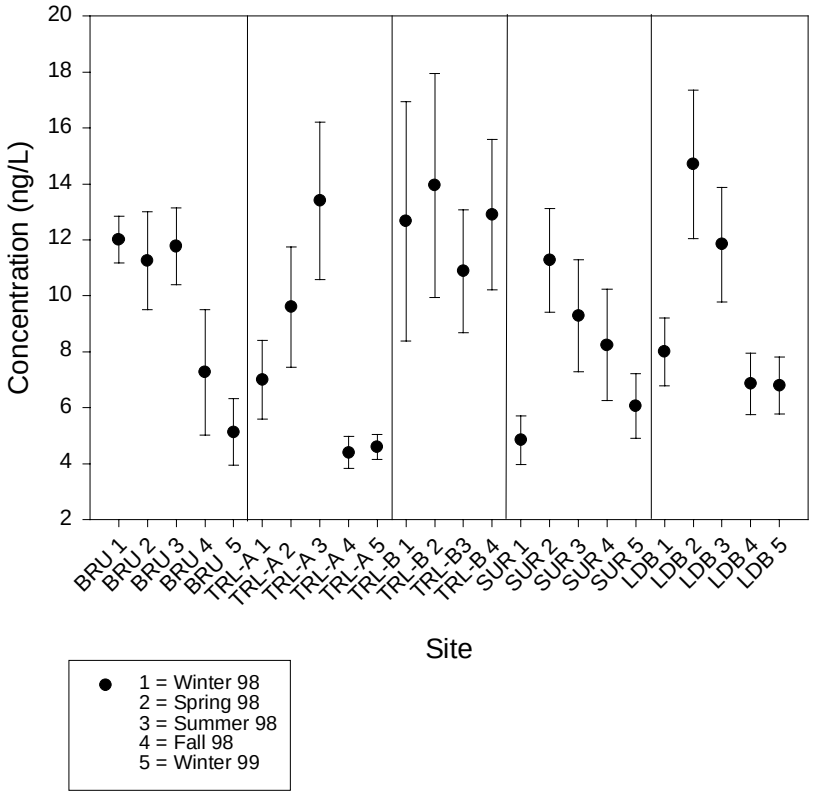


Figure 11
1998/99 Seasonal Mean Concentrations
at Southern Sites

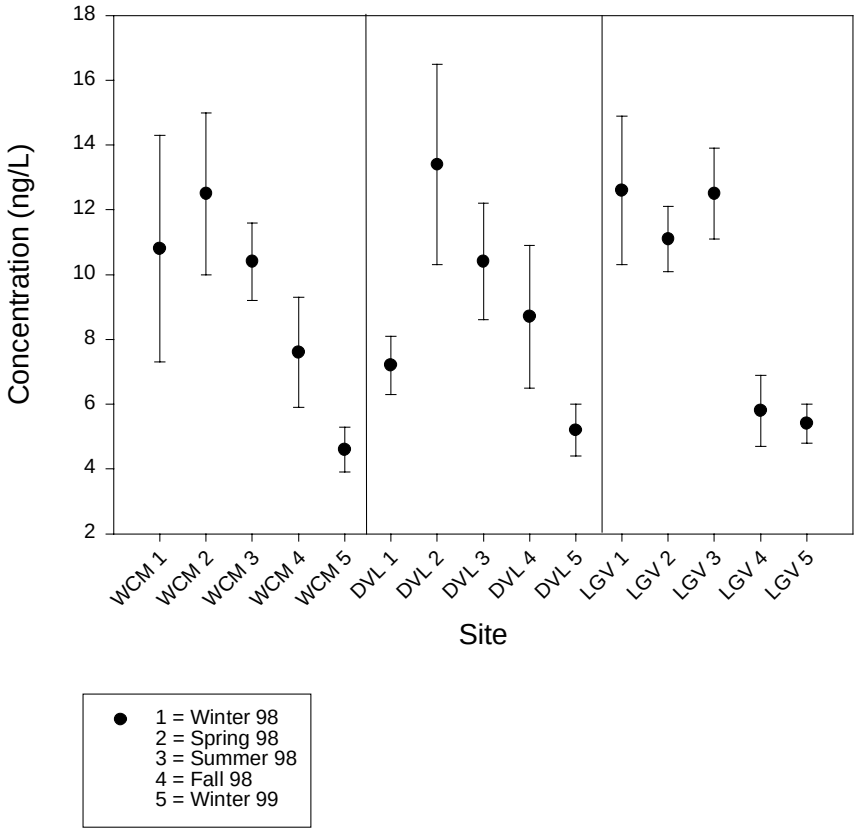


Table 3: 1998 Seasonal IVL Concentrations (ng/L)										
Site	**Winter**	*n*	**Spring**	*n*	**Summer**	*n*	**Fall**	*n*	**Winter 99**	**1998 Annual Mean** [1]
BRU	12±0.8	7	11.2±1.8	13	11.8±1.4	13	7.3±2.2	13	5.1	10.38
TRL-A	7±1.4	12	9.6±2.2	13	13.4±2.8	9	4.4±0.6	10	4.6	8.49
TRL-B	12.6±4.3	8	14±4.0	10	10.9±2.2	11	12.9±2.7	12	*	12.38
SUR	4.5±0.9	7	11.3±1.9	13	9.3±2.8	13	8.2±2.1	13	6.1	8.82
LDB	8.0±1.2	12	14.7±2.7	12	11.8±2.0	12	6.9±1.1	13	6.8	9.98
WCM	10.8±3.5	6	12.5±2.5	12	10.4±1.2	10	7.6±1.7	11	4.6	10.09
DVL	7.2±0.9	13	13.4±3.1	11	10.4±1.8	13	8.7±2.2	8	5.2	9.93
LGV	12.6±2.3	13	11.1±1.0	13	12.5±1.4	13	5.8±1.1	13	5.4	10.49
Seasonal Mean	9.34±1.1	78	12.21±0.6	97	11.31±0.5	94	7.73±0.9	93		9.84±0.37

[1] - Mean of all weekly 1998 concentrations; excludes winter 1999 deposition data

* Data not available for TRL-B in 1999.

Note – All concentration values are the mean value ± the standard error.

Based on an ANOVA, there are statistical differences among the mean seasonal concentrations of all the sites ($p \leq 0.025$). The results of a Fisher's Least-Significant-Difference (LSD) test demonstrates that mean winter seasonal concentration for all the sites is significantly less than that of spring or summer ($p \leq 0.007$ & $p \leq 0.041$), respectively. The mean seasonal concentrations of winter and fall are statistically similar, and the mean seasonal fall concentration for all of the sites is significantly less than either spring or summer ($p \leq 0.0001$ & $p \leq 0.003$), respectively.

Seasonal Deposition:

Seasonal deposition at all sites is depicted in Figure 12 and displayed in Table 4. Maximum deposition occurs either in the spring (62.5% of sites) or summer (37.5% of sites) when precipitation is greatest. Likewise, minimum deposition occurs either in the winter (75% of sites) or fall (25% of sites) during the months commonly having low precipitation amounts. Seasonal deposition values range from as little as 0.29 ($\mu g/m^2$) to as much as 4.46 ($\mu g/m^2$).

Figure 12
1998/99 Seasonal Deposition

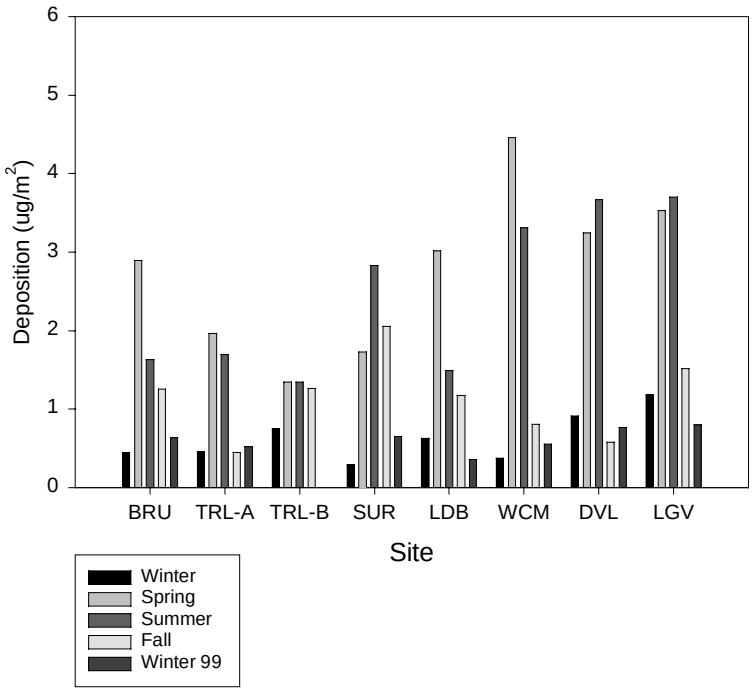


Table 4: 1998/1999 Seasonal IVL Deposition (μg/m^2)

Site	Winter	Spring	Summer	Fall	Winter 1999	1998 TOTAL [1]
BRU	0.45	2.90	1.63	1.25	0.63	6.23
TRL-A	0.46	1.56	1.69	0.45	0.52	4.16
TRL-B	0.38	1.34	1.34	1.26	*	4.32
SUR	0.29	1.73	2.82	2.06	0.65	6.90
LDB	0.62	3.02	1.49	1.18	0.36	6.31
WCM	0.37	4.46	3.31	0.81	0.55	8.95
DVL	0.91	3.24	3.67	0.58	0.76	8.4
LGV	1.18	3.53	3.70	1.52	0.80	9.93

[1] Total excludes the winter 1999 deposition data.
* Data not available for TRL-B in 1999.

A statistical comparison of the seasonal mean weekly deposition values was performed, and there is no significant difference at the 0.10 level among the sites during any of the seasons (Table 5).

Table 5: 1998/99 Seasonal Mean Weekly Deposition ANOVA Results	
Season	**($p \leq$ value)**
Winter	0.340
Spring	0.362
Summer	0.662
Fall	0.940

Comparison of Collocated Wisconsin IVL and national Mercury Deposition Network (MDN):

A table comparison of Wisconsin IVL and national MDN seasonal concentration and deposition data from three collocated monitors follows (Tables 6 &7). Generally, agreement between the two monitor types is poor in the fall and winter during periods with little or primarily frozen precipitation. Agreement improves greatly in the spring and summer.

Table 6: 1998 Seasonal Comparison of IVL and MDN Network Concentrations (ng/L)

Site	Winter		Spring		Summer		Fall	
	IVL	MDN	IVL	MDN	IVL	MDN	IVL	MDN
BRU	12±0.8	7.48	11.2±1.8	10.2	11.8±1.4	16.2	7.3±2.2	10.5
TRL-A	7±1.4	2.89 [1]	9.6±2.2	13.9 [1]	13.4±2.8	12.4 [1]	4.4±0.6	13.5 [1]
TRL-B	12.6±4.3	2.89 [1]	14±4.0	13.9 [1]	10.9±2.2	12.4 [1]	12.9±2.7	13.5 [1]
LGV	12.6±2.3	3.5	11.1±1.0	11.2	12.5±1.4	19.3	5.8±1.1	13.4

[1] - There is only one MDN monitor at Trout Lake. The A & B IVL sampling trains at Trout Lake are compared to this monitor.

Table 7: 1998 Seasonal Comparison of IVL and MDN Network Deposition ($\mu g/m^2$)

Site	Winter		Spring		Summer		Fall	
	IVL	MDN	IVL	MDN	IVL	MDN	IVL	MDN
BRU	0.45	0.74	2.90	2.33	1.63	3.94	1.25	2.02
TRL-A	0.46	0.25 [1]	1.96	1.77 [1]	1.70	3.48 [1]	0.45	1.99 [1]
TRL-B	0.75	0.25 [1]	1.34	1.77[1]	1.34	3.48 [1]	1.27	1.99 [1]
LGV	1.18	0.76	3.53	2.79	3.70	5.68	1.52	3.35

[1] - There is only one MDN monitor at Trout Lake. The A & B IVL sampling trains at Trout Lake are compared to this monitor.

Within Site Comparison between the Trout Lake A & B Sampling Trains

In order to assess inter-laboratory accuracy, a comparison between the two collocated sampling trains of the Trout Lake WIVL monitor was performed. Figure 13 depicts the WIVL design; the two juxtaposed sampling trains within the same sampler housing are visible.

Samples collected with the Trout Lake A sampling train were analyzed at the Wisconsin State Laboratory of Hygiene while samples collected on the Trout Lake B sampler were analyzed at the University of Wisconsin Limnology Laboratory at Trout Lake. Interestingly, it was found that the maximum mean concentration of all the sites in 1998 (12.38 ± 1.04 ng/L) was found on the TRL-B sampling train, while the minimum mean concentration (8.39 ± 1.04 ng/L) was measured with the TRL-A sampling train. Based on a studentized t-test, these concentrations are significantly different ($p \leq 0.022$). A linear regression performed on the TRL-A and TRL-B data produced an R^2 value of 0.336 indicating a poor relationship between 37 corresponding weekly concentration results from the two data sets (Figure 14). This discrepancy reflects the lack of inter-laboratory agreement seen in previous years. In the preceding 1995-1997 mercury data report, however, it was noted that the mean mercury concentration calculated for the TRL-B sampling train was consistently lower than the TRL-A mean mercury concentration.

Figure 13
Wisconsin IVL Passive Sampler

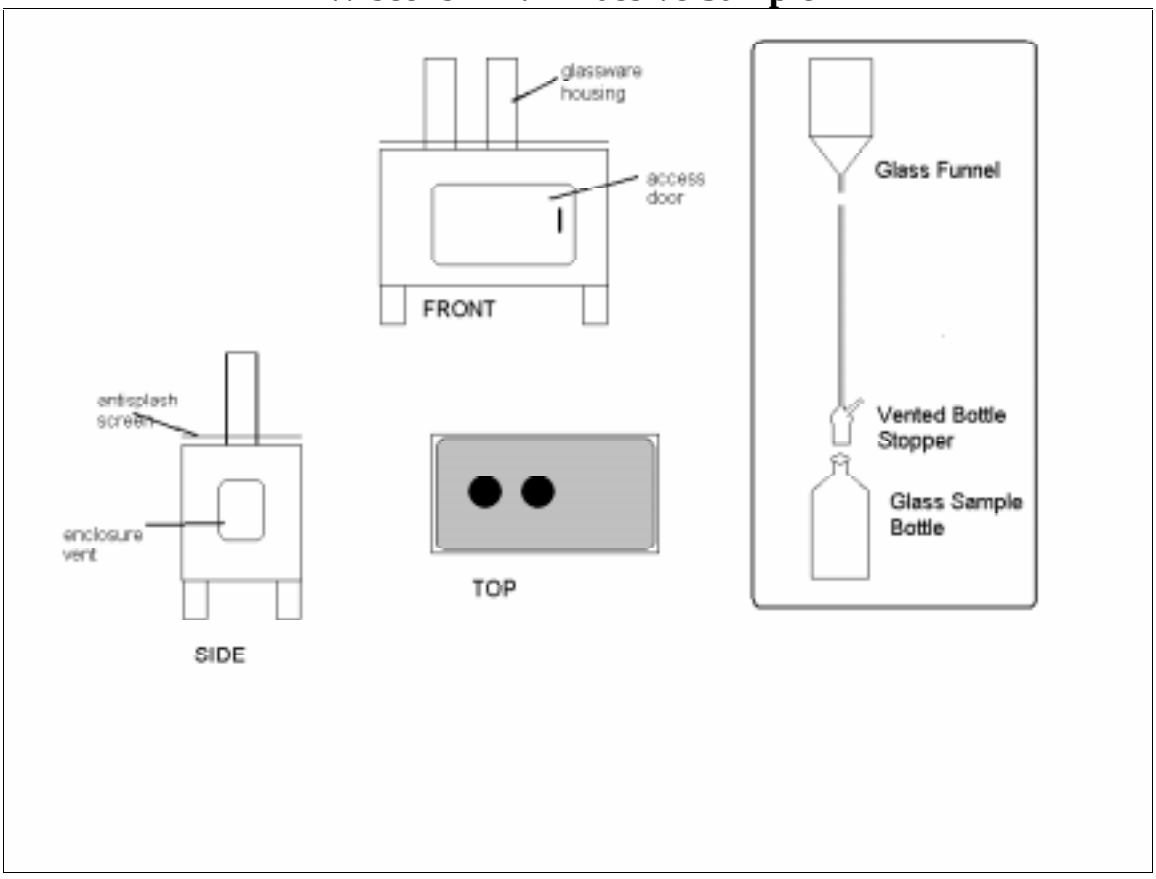
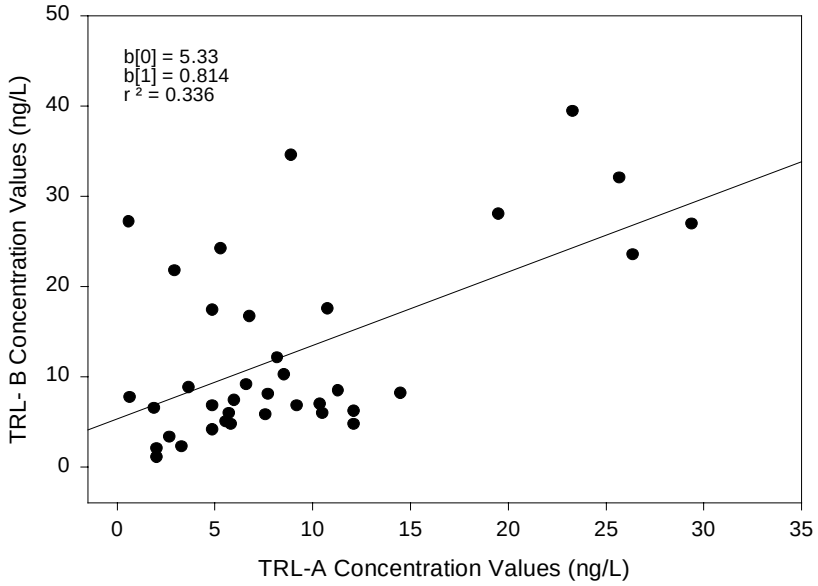


Figure 14
Linear Regression Comparison of 1998
TRL-A and TRL-B Sampler Concentrations



Data Completeness:

Data completeness in 1998 was good to excellent (Table 8), and all sites meet the EPA's 75% data completeness criterium for data analysis. Data completeness exceeds 50% at each site during all seasons. Most sites have the lowest percent complete in the winter months when sample freezing in the glass sampling train presents a problem. Brule River, the northernmost site, improved from 56% data completeness in 1997 to 88% in 1998. The mean percentage of complete samples for all sites is 87%.

Table 8: 1998 Data Completeness

Site	Season	*n*	% Complete
BRU	WI	7	54
	SP	13	100
	SU	13	100
	FA	13	100
	Annual	**46**	**88**
TRL-A	WI	12	92
	SP	13	100
	SU	9	69
	FA	10	77
	Annual	**44**	**85**
TRL-B	WI	8	61
	SP	10	77
	SU	11	85
	FA	12	92
	Annual	**41**	**79**
SUR	WI	7	54
	SP	13	100
	SU	13	100
	FA	13	100
	Annual	**46**	**88**
LDB	WI	12	92
	SP	12	92
	SU	12	92
	FA	13	100
	Annual	**49**	**94**
WCM	WI	6	46
	SP	12	92
	SU	10	77
	FA	11	85
	Annual	**39**	**75**
DVL	WI	13	100
	SP	11	85
	SU	13	100
	FA	8	61
	Annual	**45**	**87**
LGV	WI	13	100
	SP	13	100
	SU	13	100
	FA	13	100
	Annual	**52**	**100**

WI = Winter; SP = Spring; SU = Summer; FA = Fall
Note: Annual % complete is of 52 weekly samples.

References:

"Wisconsin Mercury Deposition Network Summary Report 1995 –1997" Volume 2, Publication #: PUB-AM-302-99, November, 1999.

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